

Thermal Degradation Behavior of Mechanically Alloyed Mixtures of High Density Polyethylene (HDPE) and Petroleum Coke

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Abstract

Significant quantities of waste plastics generated worldwide have resulted in a serious environmental issue. A number of recycling approaches are developed as alternatives to incineration and landfilling. The modification of polymer degradation behaviour through mechanical alloying is reported in this study. The thermal degradation behaviour of 50:50 blends of High density polyethylene (HDPE) and petroleum coke has been investigated using mechanical alloying (milling) at speeds ranging between 100 to 300 rpm and for periods up to 5 hours. Milled specimens were characterised using SEM and x-ray diffraction; and their thermal degradation behaviour was investigated using thermo-gravimetric analyser (TGA) for temperatures up to 1200°C. Whereas HDPE specimens showed a tendency towards flattening out and increased surface area during collisions in ball mills, petroleum coke particles tended to break down into smaller particles. Coke/HDPE blends showed significant microstructural evolution with increasing speeds and time including fracture, strain hardening and re-welding. X-ray diffraction results showed clear evidence for increasing amorphous component in petroleum coke without much influence on HDPE crystallinity. Thermo-gravimetric results showed a significant increase in the overall degradation and much higher weight losses associated with mechanical alloying. This study has shown that mechanical alloying could be used to speed up the thermal degradation of coke/plastic blends during pyrolysis; and this modification could be used to process plastic waste at relatively lower temperatures or over shorter time periods.

Keywords

HDPE; Petroleum Coke; Mechanical Alloying

Introduction

Global demand for plastic products has increased steadily over the past several decades and will

continue to expand in future with expanding economies. As most of the plastics cannot be easily returned to the natural carbon cycle, plastics waste constitutes a major environmental problem. Key plastic waste management methods include incineration and landfilling, both of which are associated with a number of negative environmental impacts [Westerhout 1997, Denison 1996]. Although energy is recovered during incineration, it is sometimes accompanied by the emission of harmful by-products and noxious gases. Landfilling can only be located in specific geographic circumstances, and occupy valuable space in highly populated areas and poses the threat of methane emissions. Landfilling option becomes economically as well as environmentally unviable. Recycling is considered as an important option for managing waste plastics and could play a significant role in sustainable developments in the field. In this respect, the pyrolysis of plastic materials has received much attention due to the possibility of converting these wastes into useful energy products or valuable chemicals [Sakata 1999, Predel 2000, Kaminsky 2004].

Among various types of plastic wastes, High Density Polyethylene (HDPE) constitutes a significant proportion of the total waste in the form of several products from automotive industry, toy market and various other products [Williams 1997]. HDPE is semi-crystalline and consists of macromolecules of hydrocarbons with significant intrinsic energy content and a very high calorific value [Kirchner 1996]. HDPE has a higher content of hydrogen than coals and coke [Galli 2001, Liu 1995, Sakurovs 2003]. With the aim to develop a novel recycling approach for polymeric

waste, we report an investigation on the influence of mechanical alloying on the thermal degradation behaviour of mixtures of HDPE and coke and on the carbon yield as a function of temperature. Mechanical alloying (MA) refers to high energy ball milling technique employed to process solid-state multiphase materials [Horvat 1999]. The MA is expected to induce radical chain scissions within polymer particles [Lu 1998], which could couple with coke and produce a more stable blend by grafting. The aim of this study is to develop a fundamental understanding of the influence of processing parameters of mechanical alloying on thermal degradation of HDPE and coke mixtures. Detailed investigations on 50:50 blends of HDPE with Petroleum coke were reported in this paper. The effects of milling speed and time were investigated using Scanning electron microscopy (SEM/EDS), thermo-gravimetric analysis and X-ray diffraction. Key modifications to polymer degradation behaviour were discussed.

Experimental

Powders of HDPE and Petroleum coke (PC) were separately milled for 2 hours in a tumbling ball mill with a 2:1 ball to powder ratio at 80 rpm to obtain particles of mesh size -48 to +65 (average particle size 210-300 μ) and -65 to +100 (average particle size 105-125 μ). The results of C, H, and N (wt %) carried out on CHNS analyzer (Exeter Analytical Inc. Model No. CE-440 Elemental Analyzer) are given in **Table 1**. Ball milling of 50:50 mixture of HDPE/PC was carried out in planetary mill in agate jars. Ball milling was carried out at speeds of 100, 200 and 300 rpm for times ranging between 15 and 90 min in air. A ball to powder ratio of 30:1 was used in these experiments. Some studies were also carried out at 300 rpm for periods up to 10 hours.

TABLE 1 ELEMENTAL ANALYSIS OF CONSTITUENTS

Sl. No.	Material Size: 255 \pm 45 μ	C	H
1	Petroleum coke	95.86	0
2	HDPE	85.39	14.92

Thermo-gravimetric analysis of individual constituents and alloyed blends was performed on a PerkinElmer Pyris Diamond thermal analyzer. Samples (weights ~10–15 mg) were placed in a platinum crucible and heated up to 1500°C at a heating rate of 10°C/min in nitrogen at a flow rate of 100 ml/min. The X-ray diffraction pattern (XRD) of milled powders were recorded on a Bruker AXS Diffractometer using Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation and a nickel filter at 35

kV. A scan rate of 2°/min was used to record diffraction patterns in the 2 θ range of 5–80°. The SEM-EDAX images were recorded on a Quanta Fei-200 electron microscope and the samples were coated with a thin gold layer.

Results and Discussion

Microstructural Evolution

Mechanical alloying is known to modify the microstructure of constituents through repeated welding, fracturing, and re-welding [Nesarikar 1997]. The morphology of the initial powders gets modified when subjected to ball collisions at high speeds for extended periods of time. The SEM micrographs of HDPE and petroleum coke individually milled at 80 rpm for 30 min in a tumbling ball mill are shown in **Figure 1a** and **1b** respectively.

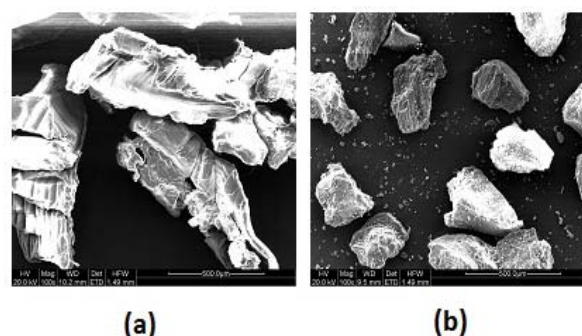


FIGURE 1 SEM MICROGRAPHS OF (a) HDPE AND (b) PETROLEUM COKE AFTER BEING INDIVIDUALLY MILLED AT 80 rpm FOR 30 min.

SEM micrographs show that the particles of HDPE, being quite ductile, were found to get flattened on milling; however, the particles of PC were found to be quite small and were similar in shape and size. SEM results for the milled mixture (PC & HDPE in 50:50 proportion) are shown in Figure 2; of which Figure 2a shows results for 200 rpm milling for 90 minutes and Figure 2b is for milling at 300 rpm. Significant differences could clearly be seen.

The ball-powder-ball collisions result in the formation of finer powder particles as seen in Figure 2a, and in the cold welding of particulates as seen in Figure 2b. The consequences of milling of powder depend on the basic characteristics of constituent particles, e.g., ductile particles end up with higher deformation with subsequently better agglomeration *i.e.*, cold welding. Whereas harder particles inhibit the re-welding processes. In Figure 2a, it can be seen that the extent of breaking increased with increment in the milling speed from 80 (for as received powder) to 200 rpm. This

would in-turn increase the contact area of different particles and enhance the inter diffusion process. Both HDPE and PC being carbon rich compounds, it was difficult to differentiate between them during SEM-EDAX analysis based on elemental distribution. An uneven distribution of finer particles of PC was observed on expanded splats of HDPE at 200 rpm for 90 min (Figure 2 a) which may be explained on the basis of the brittle nature of PC resulting in larger diffusivity of PC over HDPE sites. On the other hand, extended periods of milling help in improving the work hardening and, consequently the brittleness of the particles. Therefore, higher extents of milling can result in finer particles with harder phases.

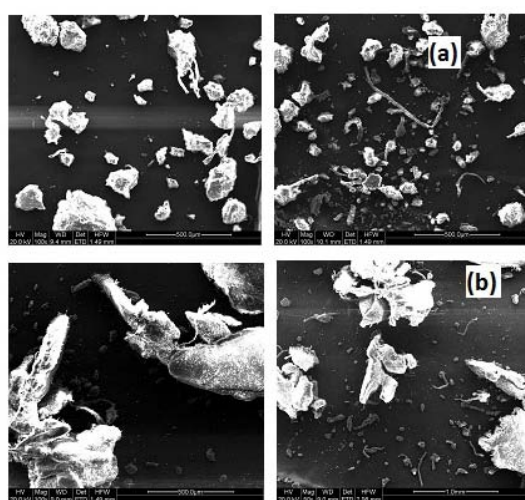


FIGURE 2 SEM MICROGRAPHS OF 50:50 BLEND OF HDPE AND PETROLEUM COKE MILLED AT SPEEDS OF (a) 200 rpm AND (b) 300 rpm FOR 90 min

In Figure 2b, the size of the particles was seen to increase on further increase in milling speed i.e., up to 300 rpm, which causes an increase in frequency of collision between ball-particle-ball and ball-particle-wall of container and helps in the agglomeration of particles rather than further breaking. It may be explained by considering that the new surfaces created due to breaking down of powder particles have high free energy and can readily be joined together by application of lower pressure. The external energy in the form of impact is responsible for the joining of the nascent surfaces, which results in the agglomerated particles. Therefore in first case (from 100 to 200 rpm), the increase in pressure helps in breaking; but in the latter case (from 200 to 300 rpm) it favors the agglomeration of particles. Similarly, the uniformity is expected to increase at higher rpm but at the same time, too fast speed is not desirable. The upper limit of rpm is dictated by the critical speed of the ball mill, because beyond this speed, the balls and the powder

will tend to stick to the container wall.

Thermal Decomposition Behaviour

DTA/TG curves of thermal decomposition of 50:50 blends of HDPE and PC are presented in Figure 3 for a range of milling speeds and times. Corresponding results for HDPE and PC have also been included for sake of comparison. In the TG curve of HDPE, the weight loss result showed that the degradation occurred almost completely in one step at 478°C. The TG curve shows that thermal degradation of HDPE started at 400°C and ended at 501°C. Two peaks 131°C and 480°C corresponding to endothermic reactions are observed in the DTA curve. The first peak corresponds to the melting of HDPE, which begins at 105°C and continues up to 160°C, without any accompanying weight loss. The second peak corresponds to the decomposition reaction. Thermal decomposition of PC suggested that almost negligible % wt. loss (i.e. 1 %) was observed in the applied temperature range (25-1200°C) and no peak was observed in the DTA curve.

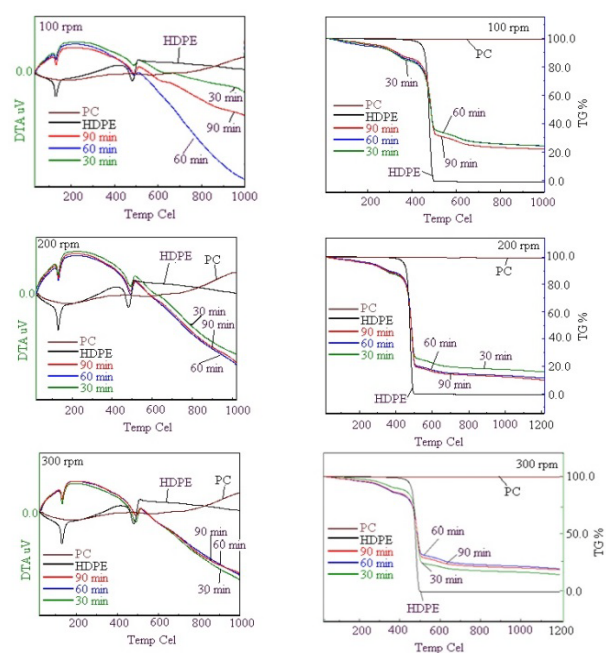


FIGURE 3 DTA/TG ANALYSIS PLOTS OF 50:50 MIXTURES OF HDPE AND PC MECHANICALLY ALLOYED FOR A RANGE OF MILLING TIMES AND SPEEDS.

The TG and DTA curves for the coke: HDPE mixture milled at speeds of 100, 200 and 300 rpm milling speed for times ranging between 30 and 90 min are shown in Figure 3. Ball milling was also carried out on individual constituents; and results for both HDPE and petroleum coke milled individually at speeds ranging from 100 to 300 rpm are also shown in the figure. Milling did not have a significant influence on their thermal degradation behaviour. The TG curves

for the mixture showed that although decomposition proceeded in one step, the temperature range of decomposition was much broader: 366-610°C which was significantly different from HDPE or coke alone. The major weight loss step occurred between 400-508°C and exhibited a total weight loss of about 80%. In DTA curve, the temperature of endothermic peaks for pure HDPE was observed at 131°C (185 mJ/mg) and 480 °C (324 mJ/mg). For mechanically alloyed mixtures of HDPE and PC for different rpm and time, the melting enthalpies for the first and second peak were less than pure HDPE and the peak temperature for second peak also shifted to 488°C. These two results indicate the presence of amorphous materials in the milled mixture [Cavalieri 2003]. These results clearly indicate the formation of mechanical alloys as the results after milling are significantly different from those expected from a 50:50 mixture.

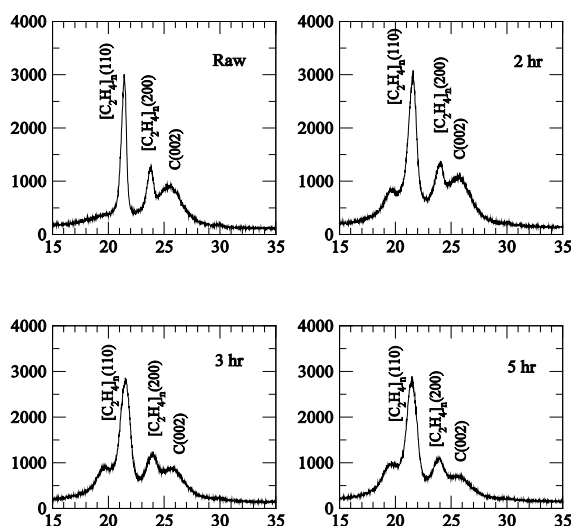


FIGURE 4 X-RAY DIFFRACTION PROFILES OF 50:50 HDPE/COKE BLENDS AFTER BEING MILLED AT 300 rpm FOR PERIODS UP TO 5 hours.

XRD Analysis

The XRD spectra of mixtures milled at 300 rpm for periods up to 5 hours is in Figure 4. The XRD spectrum of HDPE shows two major peaks at 2θ , 21.6° and 23.98° corresponding to $(C_2H_4)_n$ (110) and $(C_2H_4)_n$ (020) peaks, respectively. The XRD spectrum of PC shows a broad peak at 2θ , 25.4° corresponding to (002) graphite peak. There are three novel features in these XRD spectra. Firstly, the crystalline nature of HDPE was affected to a very small extent even though milling was carried out at fairly high speeds and for extended periods of time. HDPE peaks remained fairly sharp even after five hours, although a small flattening of peaks could be observed. Petroleum coke appeared to get affected to a much greater extent. The (002) peak height

showed a continuous decrease with milling time and has become very broad after 5 hours. Thirdly, an additional small peak was observed on ~19.5° which increased slightly with increasing time.

This result indicated that mechanical alloying resulted in reducing/destroying the crystalline order in petroleum coke. This has also resulted in enhanced reactivity as indicated by the corresponding TGA curves. There was negligible weight loss associated with 100% petroleum coke during milling at speeds ranging between 100 to 300 rpm over extended periods, and HDPE had completely degraded with negligible levels of residual carbons. The carbon yield was measured by a LECO analyser; and these materials were predominantly composed of carbon with very small levels of impurities. These results are in agreement with published literature [Uddin 1997]. Therefore, a 50:50 mixture is expected to produce an average carbon yield of ~50%. However, when mixtures of HDPE and PC were subjected to mechanical alloying, the residual weight (carbon yield) was around 20%. There were only small differences in carbon yield as a function of milling speed and time. Mechanical alloying significantly enhanced the rate of weight loss and therefore the reactivity of petroleum coke as well as that of HDPE. The rate of weight loss is linked directly to the dissociation of chemical bonds and the release of various reaction products; and it can be used as a measure of the reactivity of the carbonaceous system. A continuous weight loss was observed at low temperatures (< 450°C), where the individual constituents have originally shown no weight loss. This could be attributed to the increased surface area for HDPE particulates that were significantly flattened out during milling. The weight loss was very significant at higher temperature (> 500°C); which could be attributed to the amorphisation of petroleum coke confirmed through the corresponding XRD results. This result indicated that amorphous petroleum coke was much more reactive than crystalline coke showing significantly higher weight losses. This study has shown that the thermal degradation behaviour of petroleum coke and HDPE could be significantly modified through mechanical alloying of their blends. This modification could in turn be utilized to speed up thermal transformations in waste plastics and help develop novel approaches to their recycling.

Conclusions

The thermal decomposition behaviour of mechanically

alloyed mixtures of HDPE and Petroleum coke has been investigated using TGA and characterized using SEM and XRD. Milling time and speed are the two important variables in ball milling that control two opposite phenomenon i.e. breaking and agglomeration of particles along with phase transformation. The speeds of 100 rpm to 300 rpm and times up to 10 hours were used in this study. The TGA/XRD analysis of the various mechanically alloyed mixtures pointed towards phase transformation in the ball-milled specimens. Petroleum coke was found to undergo transition from crystalline to amorphous along with significant increases in reactivity and reduction in carbon yield. A single stage thermal decomposition of HDPE was attributed to the decomposition of organic matter from the sample. While no chemical transformations were observed in these solid state reactions, however, it is possible that synergistic effects in the gaseous or gas-solid phase may occur during thermal decomposition. This study has shown that the mechanical alloying of waste plastics with other carbonaceous materials could be used to modify their degradation behaviour.

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